VYVAL'KO, I.G.; DUSHECHKIN, A.I. [deceased]; LUSHCHEVSKAYA, G.M.; MATKOVSKIY, K.I.; SAVINOV, B.G.; SHILOV, Ye.A.; YASNIKOV, A.A.

Mechanism of the biosynthesis of isoprene compounds. Part 2. Formation of carotene pigments in the leaves of kok-saghyz. Ukr. khim. zhur. 22 no.5:655-659 '56. (MLRA 10:6)

1. Institut organicheskoy khimii Akademii nauk USSR i Institut fiziologii rasteniy i agrokhimii Akademii nauk USSR.
(Carotene) (Kok-saghyz) (Biosynthesis)

7

5

Chem

Theory of nucleophilic additions. IV. Addition of hydrogen iodide from solutions of iodides. V. G. Ostroverkhov and E. A. Shilov. *Ukrain. Khim. Zhur.* **22**, [illegible] (1956)(in Russian); cf. C.A. 51, 6515*i*.—The 2nd-order rate consts. at 25° and 35° (in l./mole min.), activation energies (in kcal./mole), and activation entropy changes (cal./degree mole) for the addn. of HI to $(MeO_2CC:)_2$ from the following iodide solns. are reported: LiI in HOAc, 0.783, 1.67, 14, −23; LiI in MeOH contg. 3.0-3.2 mole/l. HOAc (I), 0.0307, 0.059, 11.9, −35.6; KI in I, 0.0374, 0.0825, 14.4, −20.6; KI in I contg. 14.6 mole/l. H_2O, 0.0383, 0.0737 (30°), 11.0 (calcd. from 20-30°), −35.1; MgI_2 in I, 0.0334, 0.072, 14 (calcd. from 20-30°), −28.6; Et_4NI in I, 0.0288, 0.0620, 14.2, −2.8. Corrections were made for the amt. of I_2 present in the solns. *trans*-$MeO_2CCH{:}CICO_2Me$ was formed. The rate depended on the I^- concn.; the subsequent addn. of H is rapid. Of 2 proposed mechanisms, the open-chain one is considered more probable than the cyclic one, since there are no great differences in entropy change for the various cations and solvents. At 40°, $PhC{:}CCH_2NEt_2$ did not react with KI in a H_2O-HOAc-MeOH mixt.

John Howe Scott

RM MT

Inst. Org. Chem AS Ukr SSR

SHILOV, Ye.A.

On A.I. Titov's and F.L. Maklyaev's papers. Zhur. ob. khim. 26 no.8: 2365-2367 Ag '56. (MLRA 10:11)

(Olefins)

(Titov, A.I.) (Maklyaev, F.L.)

SHILOV, E., Institute of Organic Chemistry, Kiev, USSR

"The Method and the Stereochemistry of the Addition of the Hydracides HalH to Non-Saturated Compounds," a paper submitted at the 16th International Congress of Pure and Applied Chemistry, Paris, 18-24 July 1957.

SHILOV, [illegible] A.

"The use of radio-active carbon C^{14} for investigating the mechanism of biosynthesis of rubber and its concomitants in the Kok-Sagyz," a paper submitted at the International Conference on Radioisotopes in Scientific Research, Paris, 9-20 Sep 57.

USSR/Physiology of Plants. Respiration and Metabolism. I-3

Abs Jour: Ref. Zhur-Biologiya, No 1, 1958, 1142.

Author : Vyval'ko, I.G., Dushechkin, A.I., Matkovskiy, K.I., Shilov, Ye. A., Yasnikov, A.A.
Inst : none given
Title : The Formation in Kok-Sagyz Leaves of Carbonic Acid From Sugars and Acids Containing Marked Carbon

Orig Pub: Byul. po fiziol. rasteniy, 1957, No 1, 15-19.

Abstract: Water solutions of sugars and sodium salts of organic acids containing C^{14} were applied to kok-sagyz leaves (three portions over the course of three days or in one dose before the beginning of the experiment. The air was withdrawn from the plant by use of a vacuum dessicator; the carbon dioxide, absorbable in 25% NaOH, was precipitated, and the radioactivity measured in the dried $BaCO_3$ deposit. It was observed that a considerable

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USSR/Physiology of Plants. Respiration and Metabolism.

Abs Jour: Ref. Zhur-Biologiya, No 1, 1958, 1142.

quantity of $C^{14}O_2$ was isolated two or three hours after introduction of the marked elements. On the fifth or sixth day of the experiment, after application of saccharose C^{14}, α-glucose-1-C^{14}, acetic acid-1-C^{14}, pyroracemic acid-2-C^{14}, levulinic acid-1-C^{14}, levulinic acid-C^{14}, and glycocoll-1-C^{14} in darkness, more than 50% of the introduced radioactivity was isolated. 25% of the radioactivity was isolated upon introduction of -fructose-1-C^{14} and α-gluconic acid 1-C^{14}. In the experiments with levulinic acid C^{14} and pyroacemic acid-1-C^{14}, from 33-20% [sic] more $C^{14}O_2$ was isolated in the light than in darkness. As concerns the other substances, the differences between the light and dark variants were inperceptible.

Card : 2/2

SHILOV, Ye.A.

Discussion. Probl. kin. i kat. 9:274 '57. (MIRA 11:3)
(Catalysis) (Hydrogen--Isotopes)

AUTHOR: Kurakin, A. N. and Shilov, Ye. A. 73-1-7/26

TITLE: Kinetics and Mechanism of the Iodination of Aromatic Amino-Sulphonic Acids in Aqueous Solutions. (Kinetika i Mekhanizm Iodirovaniya Aromaticheskikh Aminosul'fokislot v Vodnykh Rastvorakh.)

PERIODICAL: Ukrainskiy Khimicheskiy Zhurnal, 1957, Vol. 23, No.1, pp. 31 - 53 (USSR).

ABSTRACT: The authors first give a short review of previously published work (Refs. 1 - 6). They claim that their own observations and experiments substantially supplement the theory of iodination of armotic compounds. In particular they found that not only the iodine cation but also elemental iodine can be of great importance as an iodination agent in aqueous solutions. Simpler aminobenzenesulphonic acids were selected for this experiment because they are easily soluble in water. It is shown that the simplest aniline-m-sulphonic acid iodinates extremely slowly. The 4 aminosulphonic acids (referred to hereinafter as E-acids) were: N,N-dimethylaniline-meta- and parasulphonic acids, N,N-diethylaniline-m-sulphonic acid and N-ethyl-N-phenyl-benzylamino-p-sulphonic acid. They were used in the form of their sodium salts. The whole

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Kinetics and Mechanism of the Iodination of Aromatic Amino-Sulphonic Acids in Aqueous Solutions.

is as follows:

$$- \frac{d(J)}{dt} = k_o(S^-)^2 \frac{(J)}{J-} + k_p(S^-)^2 \left(\frac{(J)}{(J-)}\right)^2 + k'_o(S^-)(HPO_4^{2-}) \frac{(J)}{(J-)}$$

$$+ \; k'_p(S^-)(HPO_4^{2-}) \left(\frac{(J)}{(J-)}\right)^2$$

where S^- is the anion of the aminosulphonic acid, (J) being the analytic concentration of iodine. The velocity of iodination of N-ethyl-N-phenylbenzylamino-p-sulphonic acid is expressed by a very simple formula where members with the constants k_o and k'_o do not appear. Neutral salts form negligible reaction accelerators. Values of the relative velocities of iodination are given for the various salts. Temperature coefficients for the salts of dimethyl- and diethylaniline-m-sulphonic acids have increased values at 10° C(4-5), for E-salts normal values (2.5 at 10° C.) Temperatures of activisation are listed. Two variants are given for the form of the transition complex: in one case the anion of the salt (i.e. the base) enters the compound of the iodising agent, in the second case the

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Kinetics and Mechanism of the Iodination of Aromatic Amino-Sulphonic Acids in Aqueous Solutions. 73-1-7/26

aminosulphonate ion (i.e. the base) appears as the proton-acceptor. There are 10 graphs, 17 tables; 27 references, 6 of which are Slavic.

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75-2-11/22

The catalytic action of amino acids and amines in organic reactions. 1: Kinetics and enolization of acetone in the presence of amino acids. (Cont.)

acceptor system. Kuzin's and Nevrayeva's mechanism could not be confirmed by these investigations. The kinetics of iodination of acetone in an aqueous solution in the presence of glycine, β-alanine and dimethylglycine were investigated (in the presence or absence of phosphoric acid salts). In all cases, at relatively large and constant concentration of acetone, the reaction proceeds according to the zero order relative to iodine. In the presence of glycine the kinetic equation

$$v = kAGG^-$$

where A = concentration of acetone;
G = glycine in the form of a bipolar ion;
G^- = glycocollate ion.

At 25 C: k = 4.0 (units: mole/l min). When both glycine and phosphate are present k' = 410 mole/l min the equation changing to

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$$v = k'AG^-\left[H_2PO_4^-\right] + kAGG^- + k_fAF$$

where F = analytic concentration of phosphate salts in

Shilov, Ye. A.

73-3-8/24

AUTHOR: Yasnikov, A. A., Shilov, Ye. A. and Matkovskiy, K. I.

TITLE: Catalytic Action of Amino Acids and Amines in Organic Reactions. 2. Kinetics and Mechanism of Enolisation of Levulinic Acid in the Presence of Glycine and Other Amino Acids. (Kataliticheskiye Deystviya Aminokislot i Aminov v Organicheskikh Reaktsiyakh. 2. Kinetika i Mekhanizm Yenolizatsii Levulinovoy Kisloty v Prisutstvii Glikokola i Drugikh Aminokislot)

PERIODICAL: Ukrainskiy Khimicheskiy Zhurnal, 1957, Vol. 23, No. 3, pp. 333-340 (USSR).

ABSTRACT: The first communication gave results of investigations on the kinetics of enolisation of acetone in the presence of amino acids. (Ref.1) Data on the kinetics of iodination of levulinic acid under the above mentioned conditions are investigated in the present article. Levulinic acid differs from acetone in the fact that it contains an acid group which occurs in 2 forms: the undissociated acid (the concentration being denoted as M) and the acid ion (M^-). M = total concentration of the undissociated acid and its ion. Investigations have shown that the iodination of levulinic acid in the presence of amino acids is limited by the enol formation stage. It can be assumed that 3- or 5-iodolevulinic acid is formed in the first instance. The structure of the iodination products

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Catalytic Action of Amino Acids and Amines in Organic Reactions. 2. Kinetics and Mechanism of Enolisation of Levulinic Acid in the Presence of Glycine and Other Amino Acids.

was not investigated. The method of measuring the rate of iodination was described in part 1. (Ref. 1). Direct titration in acidified solutions was used. This method of titration was found suitable. The synthesised levulinic acid was subjected to 2 vacuum distillations. Fractions boiling at 137 - 139°C at 10 mm Hg. Iodine sublimates from the pulverised mixture with potassium iodide. Chemically pure glycine was used for the experiment. Figure 1 shows that the rate of iodination of levulinic acid increases with increasing concentration of glycine and of the hydroxil-ion. The rate of iodination does not depend on the concentration of the iodine, G_{ab} and is, as in the case of acetone, defined by the stage of enolisation according to the kinetic equation: $v = k_0 M$. At comparatively high concentrations of levulinic acid the reaction rate is represented by straight lines. At 0.5 mole concentrations of levulinic acid, in the presence of 0.005 mole I_2 and 1.25 mole glycine a fast reaction occurs until 10% of I is spent (Fig. 2).

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Catalytic Action of Amino Acids and Amines in Organic Reactions. 2. Kinetics and Mechanism of Enolisation of Levulinic Acid in the Presence of Glycine and Other Amino Acids.

Thereafter the reaction rate decreases. In the presence of glycine the rate of enolisation of levulinic acid depends on the pH of the solution (viz. Fig. 3). At low pH (4.5 - 6) the constant k_o does not increase appreciably with increasing pH, with more alkaline solutions the rate increases sharply. Table 1 gives values for k_o and $k_2'K_2$ (where $K_2 = 2.5 \times 10^{-10}$). The addition of buffer salts (diphthalates) denoted as B in the table, does not affect appreciably the aforementioned values. The value of $k_2'K_2$ at pH 4.8 - 6 equals 1.1×10^{-8}, i.e. $k_2' = 44$. Just as in the calculation of acetone the authors found that the concentration of glycine appears in the equation as G^2. Table 2 gives the calculated values for kK_2 where

$$k = \frac{k_o \, a_{N+}}{K_2 \, G^2}$$

At pH 6 the rate of enolisation of levulinic acid increases with the concentration of the added buffer phosphate salt (F). Figure 1 and Table 3 show the relation between k_o and pH in the presence of phosphates. Several experiments

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Catalytic Action of Amino Acids and Amines in Organic Reactions. 2. Kinetics and Mechanism of Enolisation of Levulinic Acid in the Presence of Glycine and Other Amino Acids.

with various amino acids in the presence of phosphates at 25°C were carried out in order to compare their catalytic action. Table 4 gives the k_0 values for these experiments. Table 5 gives data for the relation of the rate of enolisation and the temperature. The energy of activation was 18750 cal. The kinetic equation for pH 4.5 - 9 was found to be

$$v = k_2^{\prime} M_K G^- + kMGG^- + k^{\prime} MG^- (H_2PO_4^-).$$

At 25° C: $k_2^{\prime} = 44$; $k = 0.68$; $k^{\prime} = 64$ units: mole/litre, minute). The donor - acceptor scheme of enolisation of ketones in the presence of amino acids and proton donors is discussed. There are 3 figures, 5 tables and 5 references, 2 of which are Slavic.

SUBMITTED: November, 16, 1956.

ASSOCIATION: Institute of Organic Chemistry, Academy of Sciences Ukrainian SSR. (Institut Organicheskoy Khimii AN USSR)

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[illegible]

VYVAL'KO, I.G.; DUSHECHKIN, A.I. [deceased]; LUSHCHEVSKAYA, G.M.;
MATKOVSKIY, K.I.; SAVINOV, B.G.; SHILOV, Ye.A.; YASNIKOV, A.A.

Mechanism of the biosynthesis of isoprene compounds. Part 3:
New data on rubber and carotene antecedents in kok-saghyz.
Ukr.khim.zhur. 23 no.4:516-522 '57. (MIRA 10:10)

1.Institut organicheskoy khimii AN USSR i Intitut zemledeliya
Ukrainskoy akademii sel'skokhozaystvennykh nauk.
(Biochemistry) (Kok-šaghyz)

SHILOV, YE.A,

OSTROVERKHOV, V.G.; SHILOV, Ye.A.

Investigating the theory of nucleophilic additions. Part 6: Addition of hydrazoic acid to dimethyl ether of acetylenedicarboxylic acid. Ukr. khim. zhur. 23 no.5:615-622 '57. (MIRA 10:11)

1. Insitut organicheskoy khimii AN USSSR.
(Acetylenedicarboxylic acid) (Hydrazoic acid) (Methyl ether)

SHILOV, E. A.

Distr: 4E2c(j)/4E4j/4E3d

Mechanism of rearrangement of 1-naphthalenesulfonic acid to 2-naphthalenesulfonic acid. F. M. Vainshtein and E. A. Shilov. *Zhur. Obshchei Khim.* 27, 2559-66(1957); cf. *C.A.* 49, 8845c.—The application of S^{35} tracing established that the rearrangement of $1\text{-}C_{10}H_7SO_3H$ to the 2-isomer in concd. H_2SO_4 proceeds with 70-80% exchange and 20-30% without S exchange with the environment. The exchange-involved rearrangement proceeds apparently through a stage of hydrolysis of the sulfonic acid and sulfonation of the resulting $C_{10}H_8$. The nonexchange rearrangement is either intramol. or is the result of slow diffusion of the complex formed from the sepd. sulfo group and its acceptor mol. It was shown that analytical methods for estn. of the 2-isomer are unsatisfactory for mixts. with 1-isomer, as they do not afford complete sepn. The best method is heating a 1-g. sample with 3 parts 33% HCl in a sealed ampul 1 hr. at 180°, dilg. with H_2O to remove the 2-isomer, and filtering off the hydrocarbon; the filtrate is freed of HCl by an inert gas stream at 100°; the thus obtained 2-isomer is converted to the Ba salt and sepd. from H_2SO_4.

G. M. Kosolapoff

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SHILOV, Ye.A.

Relationship between N.A. Shilov's theories and the modern concepts on the mechanism of homogeneous catalysis. Zhur.fiz.khim. 31 no.1:266 Ja '57. (MLRA 10:5)

1.Akademiya nauk USSR, Institut organicheskoy khimii, Kiyev.
(Catalysis)

Shilov, Ye. A.

20-3-40/59

AUTHORS: Shilov, Ye. A., Member of the Academy of Sciences of the AN, Ukrainian SSR, and Mironova, D. F.

TITLE: Certain Features in the Kinetics of the Addition of Hydrogen Iodide to Unsaturated Compounds. (Nekotoryye osobennosti kinetiki prisoyedineniya yodistogo vodoroda k nenasyshchennym soyedineniyam)

PERIODICAL: Doklady Akad. Nauk SSSR, 1957, Vol. 115, Nr 3, pp. 564-567 (USSR)

ABSTRACT: The authors found, that iodine accelerates the addition of HJ to cyclohexane and allylchloride, if the reaction takes place in a benzol solution. According to measurements, which have been executed, the velocity of both reactions is expressed by the equation

$$-\frac{d\,(HJ)}{dt} = k_3 M\,(HJ)\,(J_2).$$

M denoting the concentration of the unsaturated compound. The velocity of the reaction with cyclohexane is independent of temperature (at least between 4 and 30°C) (fig 1.). The temperature coefficient as well as the total activation energy equals zero. In glacial acetic acid iodine does not act as a catalysator any more. It slows down the reaction, if it is applied in a concentration commensurable with the HJ concentration. The temperature coefficient gains its normal value, which amounts to ~2,4 at 10°C (fig 2). This velocity is expressed by the equation

$$-\frac{d(HJ)}{dt} = k'_{3M}(HJ)^2, \quad k'_3 = 0{,}096 \text{ at } 20^\circ \text{ and } 0{,}23 \text{ at } 30^\circ C.$$

An addition of LiJ accelerates the reaction considerably. HJ unifies with

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20-3-40/59

Certain Features in the Kinetics of the Addition of Hydrogen Iodide to Unsaturated Compounds

SUBMITTED: February 22, 1957

AVAILABLE: Library of Congress.

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SHILOV, Ye. A. and YASNIKOV, A. (Kiev)

"Concerning the Mechanism of the Catalytic Effeect of Amino Acids on the Reactions of Carbonyl Compounds," (Section D)

report submitted for Annual Meeting East German Chemical Society, 28 Oct - 1 Nov 1958, Leipzig, G.D.R.

Inst. Organic Chem AS UkrSSR

Reel #510

Shilov, Ye.A.

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